

Covalent radii of four-co-ordinate copper(I), silver(I) and gold(I): crystal structures of $[\text{Ag}(\text{AsPh}_3)_4]\text{BF}_4$ and $[\text{Au}(\text{AsPh}_3)_4]\text{BF}_4$

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The complexes $[\text{Ag}(\text{AsPh}_3)_4]\text{BF}_4$ and $[\text{Au}(\text{AsPh}_3)_4]\text{BF}_4$ were prepared from AgBF_4 and 4 equivalents of AsPh_3 , and from equimolar quantities of $[\text{Au}(\text{AsPh}_3)\text{Cl}]$ and AgBF_4 and 3 equivalents of AsPh_3 , respectively, in dichloromethane solution. Single crystals of the two compounds are isomorphous (trigonal, space group $R\bar{3}$, $Z=6$) and contain cations with a tetrahedral $\text{Ag}/\text{Au}-\text{As}_4$ core. From the $\text{Ag}/\text{Au}-\text{As}$ distances measured at 199 K the covalent radii of four-co-ordinate silver(I) and gold(I) have been calculated using an accepted standard covalent radius for four-co-ordinate arsenic(III), $r(\text{As}^{\text{III}}) = 1.20 \text{ \AA}$; $r(\text{Au}^{\text{I}}) = 1.37 \text{ \AA}$ is found to be 6% smaller than $r(\text{Ag}^{\text{I}}) = 1.46 \text{ \AA}$. This contraction reflects the strong influence of relativistic effects on atomic radii. From other data, $r(\text{Cu}^{\text{I}})$ for four-co-ordinate copper is estimated to be 1.29 \AA .

Owing to a current debate about the relevance of relativistic effects for chemistry¹ there is growing interest in reliable structural data of compounds of the elements for which this effect is expected to be particularly pronounced. Gold is considered the 'relativistic element' *par excellence*, and therefore its atomic and molecular parameters are the subject of scrutiny in both theoretical calculations and experimental studies.

A recent investigation² of the structural chemistry of standard *two-co-ordinate* phosphine complexes of copper(I), silver(I) and gold(I) provided convincing evidence that the data on the covalent radii of the coinage metals in many handbooks and textbooks should be revised, with gold(I) definitely smaller than silver(I), and copper(I) as the smallest metal atom. These data are based on accurate X-ray diffraction studies carried out (1) under strictly comparable experimental conditions, (2) on perfectly isomorphous single crystals and (3) of compounds with the same composition and stoichiometry (ligands, counter ions). The radius of gold(I) was found to be almost 7% smaller than the radius of silver(I), agreeing very well with calculated data obtained in theoretical treatments including relativistic effects.

Several other groups have since rightly pointed out that there was scattered evidence in many of the previous papers dealing with one or the other aspect of the structural chemistry of the coinage metals which can now be taken as support of the more recent findings. It was also noted² that the new data are only valid for the *two-co-ordinate* state of the univalent metals, and that studies of the situation with higher co-ordination numbers would be highly desirable.

Directed by Bruce *et al.*³ we discovered that there was already one set of isomorphous compounds in the literature, where Cu^{I} , Ag^{I} and Au^{I} are *three-co-ordinate*. Comparison of the data shows that the radii are again Cu smaller than Au smaller than Ag, with M–P bonds very similar in length as in the *two-co-ordinate* cases. It therefore appeared that at least for co-ordination numbers two and three the results are in excellent agreement.

Four-co-ordinate complexes of gold(I) with monodentate Group 5 donor ligands are rare,^{4,5a,b} and therefore comparative studies with analogous compounds of copper(I) and silver(I) are not possible for the most common sets of ligands.

In an early, very careful study Jones⁴ showed that a representative cation such as $[\text{Au}(\text{PPh}_3)_4]^+$ appears in very different structures in salts with the $[\text{BPh}_4]^-$ anion, none of which is

really strictly four-co-ordinate. On the other hand, $[\text{Cu}(\text{PPh}_3)_4]^+$ and $[\text{Ag}(\text{PPh}_3)_4]^+$ are both truly four-co-ordinate species in their isomorphous perchlorate salts,⁶ although there are slight distortions associated with the local three-fold symmetry of the cations. The $[\text{Ag}(\text{PPh}_3)_4]^+$ cation was also structurally characterized in the nitrate⁷ and hexafluorophosphate^{8,9} salts which are again isomorphous with the perchlorate salts, and there is also an isomorphous $[\text{Cu}(\text{PPh}_3)_4]^+\text{PF}_6^-$ salt.^{9a} Yet another example, from the silver series, was encountered¹⁰ in salts $[\text{Ag}(\text{PPh}_3)_4]^+[\text{SnPh}_2(\text{NO}_3)_2(\text{Cl}, \text{NO}_3)]^-$, but markedly different distortions of the cation make comparisons less meaningful for these compounds. Compounds $[\text{CuL}_4]\text{ClO}_4$ with $\text{L} = \text{PPh}_3$, AsPh_3 and SbPh_3 were prepared, but their structures have not been determined.^{9b}

Where determined, the average M–P distances in all these Ph_3P complexes show silver to be much larger than copper, but there was no suitable species available for a comparison with gold. The only structurally confirmed homoleptic compound⁵ of the type $[\text{Au}(\text{PR}_3)_4]^+\text{X}^-$, with four independent tertiary phosphines, is $[\text{Au}(\text{PMePh}_2)_4]^+\text{PF}_6^-$, but for this example the structures of the copper and silver analogues are not known. There is reason to believe that compounds with the cation $[\text{Au}(\text{PPh}_3)_4]^+$ are actually unstable owing to steric hindrance and poor acceptor properties of the two- and three-co-ordinate precursor complexes, and will therefore not be available for comparison.

In the family of the tertiary arsine complexes the situation was less satisfactory in that structural data of homoleptic four-co-ordinate complexes were only known for silver: $[\text{Ag}(\text{AsPh}_3)_4]^+$ was structurally characterized^{11,12} with the anions $[\text{SnPh}_2(\text{NO}_3)_2(\text{Cl}, \text{NO}_3)]^-$ and $[\text{Sn}_2\text{Ph}_2(\text{NO}_3)_4(\text{OH})_2(\text{MeCN})_2]^{2-}$. These are isomorphous with each other, and also with the PPh_3 analogues.

The perchlorate salt with the cation $[\text{Au}(\text{AsPh}_3)_4]^+$ was prepared by Parish *et al.*¹³ and investigated by ¹⁹⁷Au Mössbauer spectroscopy (at 4 K). From the zero quadrupole splitting of the gold 'resonance' (isomeric shift: -0.39 mm s^{-1} relative to gold foil) the authors concluded that the metal atom is in a highly symmetrical, most probably tetrahedral, environment in this complex, but the structure has not been determined.

In the present paper we now report the synthesis and structure of $[\text{Au}(\text{AsPh}_3)_4]^+\text{BF}_4^-$ and its isomorphous silver(I) analogue. Our results provide a unique chance unambiguously to determine the relative covalent radii of the two heavier coinage metals in their *four-co-ordinate* state. It should be

Table 1 Crystallographic data for $[\text{Ag}(\text{AsPh}_3)_4]^+ \text{BF}_4^-$ **1** and $[\text{Au}(\text{AsPh}_3)_4]^+ \text{BF}_4^-$ **2**

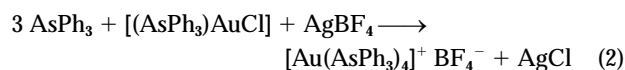
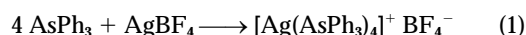
Compound	1	2
Empirical formula	$\text{C}_{75}\text{H}_{60}\text{AgAs}_4\text{BF}_4$	$\text{C}_{75}\text{H}_{60}\text{AuAs}_4\text{BF}_4$
<i>M</i>	1419.56	1508.66
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}$ (no. 148)	$R\bar{3}$ (no. 148)
<i>a</i> /Å	14.291(1)	14.245(1)
<i>b</i> /Å	14.291(1)	14.245(1)
<i>c</i> /Å	51.456(6)	51.467(3)
α /°	90	90
β /°	90	90
γ /°	120	120
<i>U</i> /Å ³	9101.1(14)	9044.2(6)
ρ_{calc} /g cm ⁻³	1.542	1.662
<i>Z</i>	6	6
<i>F</i> (000)	4272	4464
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	25.3	47.7
<i>T</i> /°C	−74	−74
Diffractometer	Enraf-Nonius	Enraf-Nonius
Scan type	CAD4	CAD4
<i>hkl</i> Range	ω - θ −17 ≤ <i>h</i> ≤ 0, 0 ≤ <i>k</i> ≤ 17, −63 ≤ <i>l</i> ≤ 63	ω 0 ≤ <i>h</i> ≤ 17, −17 ≤ <i>k</i> ≤ 0, −63 ≤ <i>l</i> ≤ 63
Measured reflections	6920	8372
Unique reflections	3981	3952
Used reflections	3969	3952
<i>R</i> _{int}	0.0502	0.0300
Refined parameters	266	254
H-atoms (found/calc.)	0/60	0/60
Absorption correction	Empirical	DIFABS ¹⁷
<i>T</i> _{min} , <i>T</i> _{max}	0.8156, 0.9978	0.942, 1.000
<i>R</i> 1 ^a [<i>F</i> _o ≥ 4σ(<i>F</i> _o)]	0.0502	0.0407
<i>wR</i> 2 ^a (used reflections)	0.1154	0.0887
Weighting scheme ^a	<i>a</i> = 0.0409, <i>b</i> = 70.7311	<i>a</i> = 0.0000, <i>b</i> = 222.8159
ρ_{fin} (max, min)/e Å ⁻³	+0.79, −0.60	+3.78, −2.88 ^b

^a $R1 = \sum (|F_o| - |F_c|)/\sum |F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2$, $w = 1/2\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$. ^b Residual electron densities located at the Au atom.

noted that $[\text{Au}(\text{SbPh}_3)_4]^+$ is also known and can be considered for further comparative studies.^{14–16}

Results

The compounds $[\text{Ag}(\text{AsPh}_3)_4]\text{BF}_4$ and $[\text{Au}(\text{AsPh}_3)_4]\text{BF}_4$ are readily synthesized from the reaction of an excess of triphenylarsine and the metal tetrafluoroborates [equations (1) and (2)].



For this purpose, gold(i) tetrafluoroborate is prepared *in situ* from (triphenylarsine)gold(i) chloride and AgBF_4 . The products are obtained in high yield as colourless crystals with high melting points [299–300 °C (Ag), 268–269 °C (Au), with decomposition], stable to air and moisture, soluble in dichloromethane, trichloromethane and tetrahydrofuran, but insoluble in diethyl ether and hydrocarbon solvents. The solutions in CDCl_3 show a single set of phenyl resonances in the ¹H and ¹³C NMR spectra, and microanalysis data confirm the proposed composition (see Experimental section). In order to rule out isomorphous substitution of gold by silver in $[\text{Au}(\text{AsPh}_3)_4]\text{BF}_4$, which was prepared using AgBF_4 [equation (2)], the samples were analyzed for silver, but no such impurities were found.

Single crystals were grown by layering dichloromethane solutions with diethyl ether. At 199 K these crystals are isomorphous [trigonal, space group $R\bar{3}$ (no. 148), *Z* = 6] with very

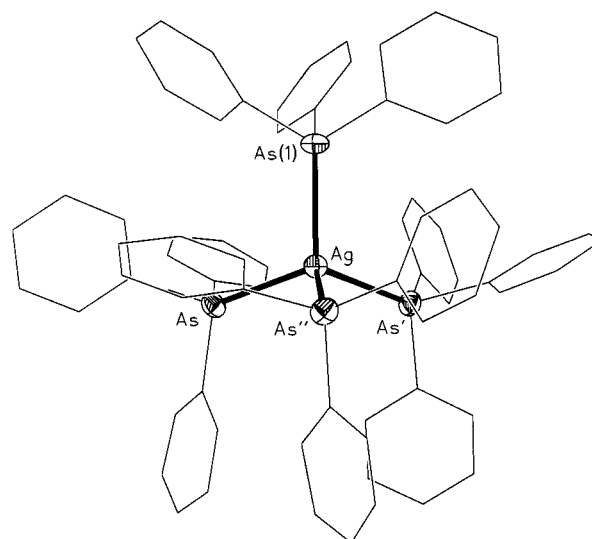


Fig. 1 Structure of the cation $[\text{Ag}(\text{AsPh}_3)_4]^+$ in complex **1** (ORTEP,¹⁸ 50% probability ellipsoids; phenyl hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ag–As(1) 2.6451(10), Ag–As 2.6578(5); As–Ag–As(1) 109.01(2), As–Ag–As' 109.92(2)

similar dimensions of the unit cells (Table 1). The lattice is composed of tetrafluoroborate anions and tetrakis(triphenylarsine)metal(i) cations, which show no conspicuous sub-van der Waals contacts.

Crystallographically the cations have only three-fold symmetry, but in both cases (*M* = Ag or Au) the structure of the MA_4 cores deviates only very slightly from regular tetrahedral symmetry. There are also no anomalies regarding the dimensions of the triphenylarsine ligands.

The cations of the silver compound show some disorder in the crystal, but the site occupation factor (s.o.f.) for the second orientation is only 7% and could be accounted for in a satisfactory way in the refinement. The central silver atom is not disordered (s.o.f. 100%). For both compounds the boron atoms of the anions are located on $\bar{3}$ centers, and the anions are therefore disordered in an analogous manner.

The high symmetry of the environment of the gold atoms in the lattice of $[\text{Au}(\text{AsPh}_3)_4]\text{BF}_4$ is in excellent agreement with the Mössbauer results (see above).¹³ The low electrical field gradient at the centre of the AuAs_4 tetrahedron leads to the observed zero quadrupole splitting.

Discussion

The structural data of the $[\text{Ag}(\text{AsPh}_3)_4]^+$ cation in the BF_4^- salt (Fig. 1) agree very well with the geometry of the same cation in the three stannates already in the literature.^{11,12} This agreement gives confidence that the data are indeed intrinsic values not influenced significantly by the environment in the crystal. The average Ag–As distance in the BF_4^- salt [this work: 2.6546(6) Å, from Ag–As(1) 2.6451(10) and Ag–As 2.6578(5) Å (×3)] is in the range of the standard deviations for the other three examples and is perhaps presently the most accurate value. Deviations of the As–Ag–As bond angles [As–Ag–As(1) 109.01(2)° (×3) and As–Ag–As' 109.92(2)° (×3)] from the standard value for the ideal tetrahedron [109.48°] are very small indeed, suggesting again that there is no meaningful distortion induced by neighbouring components of the lattice.

For the dimensions of the $[\text{Au}(\text{AsPh}_3)_4]^+$ cation in the BF_4^- salt (Fig. 2) there are no reference data from salts with other anions. The average Au–As distance [2.5827(7) Å, from Au–As(1) 2.5663(10) and Au–As 2.5882(6) Å (×3)] is smaller than the Ag–As distance in the silver-centered cation (above) by 0.072 Å. Assuming that the covalent radius of arsenic is the same for both compounds, and using textbook datum of

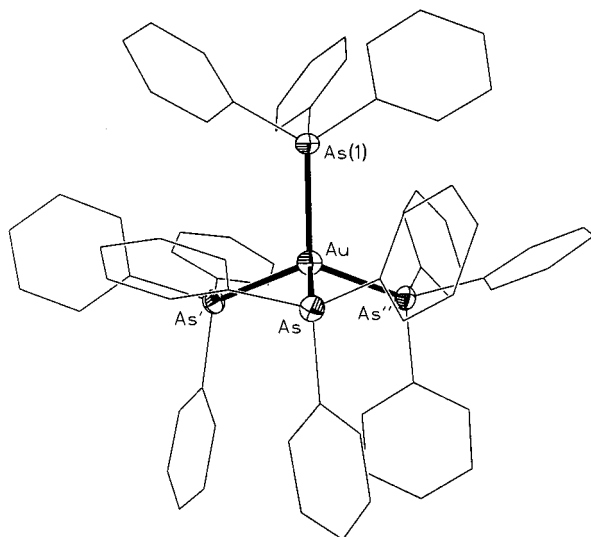


Fig. 2 Structure of the cation $[\text{Au}(\text{AsPh}_3)_4]^+$ in complex **2** (ORTEP, 50% probability ellipsoids; phenyl hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): Au–As(1) 2.5663(10), Au–As 2.5882(6); As–Au–As(1) 109.36(2), As–Au–As' 109.58(2)

$r(\text{As}) = 1.20 \text{ Å}$ for four-co-ordinate arsenic as the presently accepted value,¹⁹ the covalent radius of four-co-ordinate gold(i) (1.366 Å) is thus found to be *ca.* 6% smaller than the covalent radius of four-co-ordinate silver(i) (1.455 Å).

This result agrees well with the trend observed in two- and three-co-ordinate complexes (Introduction), which clearly indicates that silver is the larger of the two metals, and confirms the data of pertinent calculations.^{20,21}

In the absence of structural data of an isomorphous copper(i) arsenic compound, no direct comparison of the radii of all three coinage metals can be made. The data of several pairs of Cu/Ag compounds with other ligands^{5–7,9} leave no doubt, however, that copper(i) is the smallest of the coinage metals also in a four-co-ordinate environment. The covalent radius for Cu^{I} is estimated to be 1.29 Å. With this entry, the radii of the univalent Group 11 metals should be tabulated in reference treatises as: (a) two-co-ordinate:² Cu: 1.13, Ag: 1.33, Au: 1.25 Å. (b) four-co-ordinate: Cu: 1.29, Ag: 1.46, Au: 1.37 Å. These values are based here on currently accepted covalent radii of four-co-ordinated P^{III} (1.11 Å) and As^{III} (1.20 Å), but similar data are also found for complexes with isocyanide²² or ketimine ligands,²³ where carbon or nitrogen atoms are the donor sites, respectively.

Experimental

Stringent precautions were taken to exclude moisture from the solvents and reactants, as well as from the glassware employed throughout the investigation. All experiments were carried out under a purified nitrogen atmosphere.

The compound $[\text{Au}(\text{AsPh}_3)\text{Cl}]$ was prepared by following the literature procedure.²⁴ Other starting materials, AsPh_3 and AgBF_4 , were commercially available.

Proton (399.8 MHz) and $^{13}\text{C}\{-^1\text{H}\}$ (100.5 MHz) NMR spectra were recorded on a JEOL GX 400 Fourier-transform NMR spectrometer using SiMe_4 as internal standard. Microanalyses of the compounds were performed in-house by combustion and atomic absorption spectroscopic (AAS) techniques.

Preparations

Tetrakis(triphenylarsine)silver(i) tetrafluoroborate, $[\text{Ag}(\text{AsPh}_3)_4]\text{BF}_4$. To a suspension of AgBF_4 (66 mg, 0.34 mmol) in dichloromethane (20 cm^3), AsPh_3 (415 mg, 1.36 mmol) was added and the reaction mixture was stirred for 3 h. After removing 10 cm^3 of dichloromethane under vacuum, the product

(433 mg, 90%) was obtained as colourless crystals by layering the resulting solution with diethyl ether (20 cm^3). M.p. 299–300 $^\circ\text{C}$ (decomp.) (Found: C, 60.78; H, 4.43; Ag, 7.70. $\text{C}_{72}\text{H}_{60}\text{AgAs}_4\text{BF}_4$ requires C, 60.91; H, 4.22; Ag, 7.60%). NMR: ^1H (CDCl_3) δ 7.35 (4 H, t, $J_{\text{HH}} = 7.32$, *para*-Ph), 7.07 (8 H, t, $J_{\text{HH}} = 7.7$, *meta*-Ph) and 7.01 (8 H, d, $J_{\text{HH}} = 7.0$ Hz, *ortho*-Ph). $^{13}\text{C}\{-^1\text{H}\}$ (CDCl_3) δ 134.78 (s, *ipso*-C), 133.28 (s, *para*-C), 129.82 (s, *meta*-C) and 129.26 (s, *ortho*-C).

Tetrakis(triphenylarsine)gold(i) tetrafluoroborate, $[\text{Au}(\text{AsPh}_3)_4]\text{BF}_4$. A solution of AgBF_4 (32.6 mg, 0.16 mmol) in tetrahydrofuran (thf) (5 cm^3) was added with stirring to a clear solution of $[\text{Au}(\text{AsPh}_3)\text{Cl}]$ (90 mg, 0.16 mmol) in dichloromethane (10 cm^3) and stirring was continued for 15 min at room temperature. A solution of AsPh_3 (153 mg, 0.50 mmol) in dichloromethane (10 cm^3) was then added to the resulting reaction mixture and stirred at ambient temperature for 3 h. Separation of precipitated AgCl by filtration, followed by removal of volatiles under reduced pressure (25 $^\circ\text{C}$, 0.8 Torr \approx 106.6 Pa) afforded the product (237 mg, 95%). The product was crystallised by dissolving in dichloromethane and layering with diethyl ether. M.p. 268–269 $^\circ\text{C}$ (decomp.) [Found: C, 57.07; H, 4.06; Au, 13.10. The compound contains no significant amounts of silver (as determined by AAS). $\text{C}_{72}\text{H}_{60}\text{As}_4\text{AuBF}_4$ requires: C, 57.33; H, 3.98; Au, 13.06%]. NMR: ^1H (CDCl_3) δ 7.39 (4 H, t, $J_{\text{HH}} = 7.5$, *para*-Ph), 7.15 (8 H, t, $J_{\text{HH}} = 7.5$, *meta*-Ph) and 7.06 (8 H, d, $J_{\text{HH}} = 7.3$ Hz, *ortho*-Ph). $^{13}\text{C}\{-^1\text{H}\}$ (CDCl_3) δ 135.01 (s, *ipso*-C), 133.09 (s, *para*-C), 130.30 (s, *meta*-C) and 129.38 (s, *ortho*-C).

Crystallography

Suitable crystals of the compounds were sealed into glass capillaries and used for measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Diffraction intensities were corrected for Lorentz-polarization and absorption effects (empirically). The structures were solved by direct methods and refined by full-matrix least-squares calculations²⁵ against F^2 . The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized positions and allowed to ride on their corresponding carbon atom. Their isotropic thermal parameters were tied to that of the adjacent carbon atom by a factor of 1.5. The boron atoms (s.o.f. 0.17) of the tetrafluoroborate anions are located at centres of $\bar{3}$ symmetry and the anions are therefore crystallographically disordered. The cation in the silver compound is disordered in two positions with very different site occupation factors (s.o.f. 0.93 and 0.07, respectively). The silver atom shows no sign of disorder (s.o.f. 1). For the molecule with the low s.o.f. only the arsenic atoms could be found and successfully refined. Important interatomic distances and angles are given in the corresponding figure captions. Experimental details are summarized in Table 1.

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